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Photon-stimulated desorption of halogens

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Abstract

Photon-stimulated desorption of positive halogen ions is studied for systems than span a range of bond ionicities. It is found that only excitations of cation core-level electrons lead to ion desorption for very ionic systems, while only excitations of anion core electrons produce ions from more covalently bonded materials. For systems of intermediate bonding character, both cation and anion excitations can lead to ion desorption. These observations are explained within the context of Auger-stimulated desorption combined with nuclear motion.

1. Introduction

Studies of the stimulated desorption of halogen ions have been some of the most useful in delineating desorption induced by electronic transitions (DIET) mechanisms [1–3]. Because of the large electronegativity of halogens, bonding to a substrate is fairly ionic. This leads to a high positive ion yield through an Auger-stimulated desorption (ASD) process that begins with the removal of a core electron. Following core excitation, an Auger process fills the core hole, thus removing a second electron. If this results in a long-lived repulsive state, in that the two holes are maintained on the anion for a sufficient length of time, then ion desorption can occur.

In this work, photon-stimulated desorption (PSD) data are presented for positive halogen ions originating from substrates that span a range of bond ionicities. It is shown that only excitations of cation core electrons lead to positive ion desorption for very ionic systems, while only anion excitations are active for more covalently bonded materials. For systems of intermediate bonding

character, both cation and anion excitations can lead to ion desorption. These observations are explained within the context of ASD combined with the effects of nuclear motion.

2. Experimental

These experiments were performed on beamlines UV-8a and UV-8b at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. The photodesorbed ions were collected with an ellipsoidal mirror analyzer operating in angle-integrated mode [4]. Si samples were cleaned by standard techniques and soft X-ray photoelectron spectroscopy (SXPS) of the valence band and Si 2p level was used to ascertain sample cleanness and order [5]. Exposures and evaporations were performed after transferring the samples under ultra-high vacuum to a separate chamber. SXPS was then further used as a measure of surface composition after reaction. All measurements were performed with the samples at room temperature.

3. Results and discussion

CaF_2 is an ionic solid, in which an ordered array of F-center defects is readily formed by irradiation with VUV photons [6]. The PSD yield of F^+ ions desorbed from CaF_2 is shown as a function of photon energy in the vicinity of the Ca 3p and F 2s excitations in Fig. 1. The CaF_2 surface was prepared by evaporation onto

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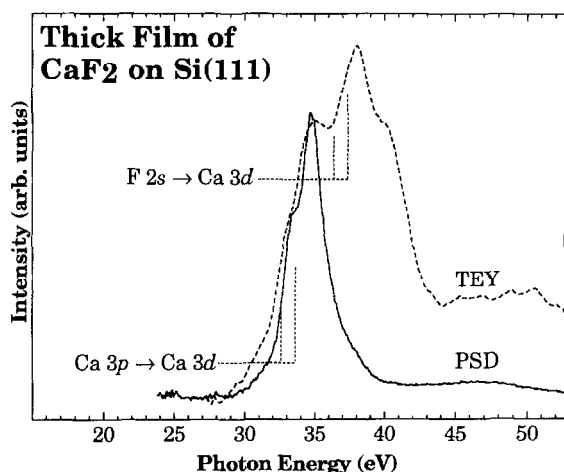
Fig. 1. PSD and TEY spectra collected from a thick film of CaF_2 grown on Si(1 1 1). The PSD scan was performed by collecting all ions that desorbed over all angles as a function of photon energy, while the TEY scan was performed by collecting all the emitted electrons as a function of photon energy. The vertical lines indicate the onsets of particular electronic transitions.

a Si(1 1 1) substrate, as described elsewhere [7–9]. The CaF_2 film was sufficiently thick that photoelectrons arising from the substrate and interface were not visible, while it was sufficiently thin that problems due to sample charging did not interfere with the measurements. In the PSD spectrum shown in Fig. 1, there is a sharp doublet peak, centered near 34 eV, that is responsible for most of the ion yield from this system [8, 9]. Also shown in the figure is the total electron yield (TEY), which provides the absorption spectrum of the material. The TEY curve shows a peak that roughly corresponds to the PSD data, but contains additional structure at ~ 38 eV.

From SXPS measurements of the core-level binding energies [7, 9], and from calculations of the density of states for CaF_2 [10], the PSD doublet can be assigned to the transition of Ca 3p core electrons in bulk CaF_2 to maxima in the unoccupied density of final states [8]. Since this is the lowest energy transition that produces ion PSD, it is concluded that an initial excitation of the Ca cation directly results in F^+ ion desorption.

The additional structure seen in the TEY spectrum corresponds to excitations of the F 2s core level, since F 2s is located about 4 eV higher in binding energy than Ca 3p [7]. Because this transition is seen in the TEY spectrum, but not in PSD, it can be concluded that initial excitations of the F anion do not lead to ion desorption [8, 9].

This result is understood as follows. The ionic CaF_2 crystal is initially in a Ca^{2+}–F^{1-} ground state configuration. After an initial cation excitation, the oxidation state configuration becomes Ca^{3+}–F^{1-}, which is more attractive than the ground state. Thus, providing that the hole is

maintained on the Ca cation for a sufficiently long time with respect to the lattice vibration period, there will be a shortening of the Ca–F bond. If, however, the initial excitation was of the F anion, then the oxidation state distribution produced is Ca^{2+}–F^0, for which there is less attraction than even in the ground state. In either case, if the core hole is filled via an Auger process, it will be inter-atomic following cation excitation and intra-atomic following anion excitation, since the electron which fills the core hole must come from the electron-rich anion. After either type of Auger decay, the system will be in a repulsive Ca^{2+}–F^{1+} configuration, from which F^+ ion desorption may occur. The Ca–F bond length at the time that the repulsive state is created will differ, however, depending on where the initial excitation occurred. The fact that only cation excitations lead to ion PSD shows that a reduced bond length is necessary in order to provide sufficient repulsion to achieve ion desorption.

A related system, but one that is less ionic than CaF_2, is F bonded directly to Si. A surface with slightly less than 1 monolayer of adsorbed F was prepared by exposure of clean Si(1 1 1)-7 × 7 to 50 L (1 L $= 10^{-6}$ torr s) of XeF_2, which produces a surface covered primarily with SiF and SiF_3 [11]. The excitations that give rise to F^+ ion desorption are illustrated in Figs. 2 and 3.

Fig. 2 shows the excitations that occur in the vicinity of the Si 2p absorption edge. The curve labeled (a) in Fig. 2 shows the PSD spectrum, while the TEY spectrum, which indicates the absorption that occurs within the Si substrate, is shown in curve (b). The major features in the bulk absorption spectrum (b), whose onsets are indicated

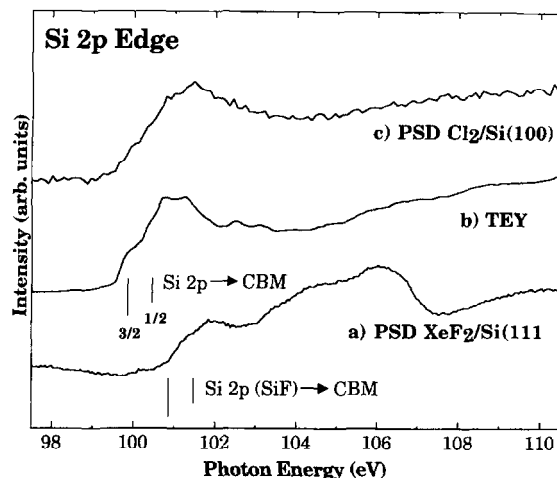Fig. 2. PSD and TEY spectra collected in the vicinity of the Si 2p edge from XeF_2- and Cl_2-exposed Si surfaces. The XeF_2-exposed Si(1 1 1)-7 × 7 surface was reacted with 50 L of XeF_2 at room temperature. The Cl_2-exposed Si(1 0 0)-2 × 1 surface was first saturated with Cl_2 gas and then annealed to 630°C in order to remove any residual F-contamination. The vertical lines indicate the onsets of particular electronic transitions.
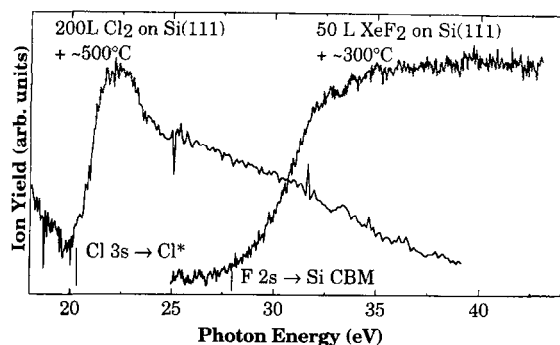
III. ADSORBED LAYERS

Fig. 3. PSD spectra collected near threshold from XeF_2- and Cl_2-exposed Si(1 1 1) surfaces which were annealed, as indicated. The vertical lines indicate the onsets of particular electronic transitions.

by vertical tick marks, are the edges at ~ 99.9 and 100.5 eV, which are due to absorption from the $\frac{3}{2}$ and $\frac{1}{2}$ spin–orbit split components of the Si 2p core-level to the Si conduction band minimum (CBM) [12, 13]. The PSD spectrum, on the other hand, has its features shifted higher in photon energy than those of the TEY. This shift indicates that the photon absorption which leads to ion desorption occurs locally at the Si atoms that are directly attached to F [4, 14], as the binding energy of the 2p level shifts by about 1 eV from that of substrate Si for each attached F atom [11]. The edge at ~ 101 eV thus represents absorption at the 2p edge of the Si atom of an SiF group, while the edge at ~ 104 eV results from photon absorption by SiF_3 groups. Note that the peak at ~ 106 eV is due to excitation from the SiF_3 Si 2p level to a σ^* molecular orbital state present at these quasi-molecular SiF_3 surface sites [4, 14].

Fig. 3 shows the PSD ion yield in the vicinity of the threshold for a Si surface first exposed to 50 L of XeF_2 and then annealed to 300°C. Such a surface is terminated solely by SiF groups [4, 14]. As is seen, the ion yield shows a threshold at ~ 28 eV, which results from excitation of a F 2s electron to the Si CBM [15].

The observation of direct PSD at the Si 2p edge shows that cation excitations do give rise to ion desorption for F bonded to Si, while the threshold behavior is a clear indication that anion excitations also induce ion PSD. Note that, in addition, excitations of the F 1s level have been shown to induce ion desorption [16]. Furthermore, in systems with a similar amount of charge transfer from cation to anion, such as GaF_3 [17], both cation and anion excitations are PSD active.

Although the mechanism involved in F^+ PSD from Si may involve some inward motion of the bound F atom prior to Auger decay, such an inward motion may not be an essential part of the desorption mechanism. Instead, consider that in a system such as this, which is not purely ionic, the electron density is not localized at the anion

sites, as in CaF_2, but rather along the bonds joining the Si and F atoms. Thus, when Auger de-excitation occurs, it is the bonding electrons themselves that are removed, thereby leading to the highly repulsive condition necessary for ion desorption.

Partially ionic systems will not always behave in this manner, however, as the degree of localization of charge with respect to the cation and anion is a sensitive function of the relative electronegativities of the constituent elements. An even more covalently-bonded system than F–Si is that of Cl bound to Si [18]. The yield of Cl^+ ions produced by photon absorption is also indicated in Figs. 2 and 3. These surfaces were prepared by exposing clean Si substrates to Cl_2 gas and then lightly annealing to remove any residual F contamination that might interfere with the PSD measurements [19].

In Fig. 2, it is seen that the PSD spectrum for Cl^+ emission mimics the TEY spectrum. This is an indication that a direct mechanism does not occur for this system following cation excitation [19]. Instead, the ions desorbed at the Si 2p edge are produced indirectly as an consequence of photon absorption in the substrate. This absorption produces secondary electrons that then induce PSD by direct excitation of a lower-lying core level [20].

For the Cl/Si system, there is only one lower energy excitation that produces ions, as shown by the threshold Cl^+ ion yield in Fig. 3. A transition is observed at ~ 20 eV, which corresponds to the excitation of Cl 3s electrons to Cl* antibonding levels, which are known to exist at about 5–7 eV above the CBM from both calculations [21] and constant initial state photoemission measurements [22]. Note that the transition from the Cl 3s level to the Si CBM does not give rise to Cl^+ ions, as it occurs at too low of an energy to both overcome the ionization potential of Cl and break the Cl–Si bond with a single photon [19].

Thus, it is seen that only anion excitations give rise to ion desorption for the Cl–Si system. While it appears that similar mechanisms exist for producing positive halogen ions following anion excitation of either F or Cl, there are clear differences in the behavior of these systems following cation excitation.

The differences between F^+ and Cl^+ PSD from Si via cation excitation are explained in the context of ASD, as follows. Assuming that we are considering only the monohalide species, the ground state is $Si^{1+}-X^{1-}$. When a Si cation is excited, the oxidation state distribution changes to $Si^{2+}-X^{1-}$. The Si core hole may be filled by either inter- or intra-atomic Auger decay. Following an inter-atomic decay, the repulsive $Si^{1+}-X^{1+}$ state is produced, from which ions may desorb. For an intra-atomic decay, however, the system will return to the ground state without ever forming a repulsive configuration. Hence, an intra-atomic Auger decay does not lead to ion desorption. In the case of F bound to Si, there is little electron

density in the vicinity of the Si atom due to the large electronegativity of F. Thus, the intra-atomic channel for filling a Si core hole is suppressed and the inter-atomic process dominates. For Cl–Si, on the other hand, the bonding is less ionic and, therefore, there is more electron density associated with the Si atom. Thus, the Si 2p hole can be filled by an intra-atomic process, which essentially quenches the desorbed ion yield. Since the intra-atomic process is expected to be faster than the inter-atomic process, even if there were a comparable number of electrons available for each, the intra-atomic process would dominate. Hence, there is little direct Cl$^+$ ion yield following Si 2p excitation.

4. Summary

Photon-stimulated desorption of positive halogen ions has been investigated for a number of systems that span a range of bond ionicities. From the ionic CaF$_2$ surface, F$^+$ ions are produced after direct excitation of cation Ca 3p core electrons, and not after excitation of the anion F 2s level. This is a consequence of an inward nuclear motion that occurs after core excitation and prior to Auger decay. This motion, which is necessary to achieve sufficient repulsion to produce ion desorption, only occurs after cation excitation. For less ionically bonded systems, on the other hand, the bonding electrons are located between the cation and anion so that nuclear motion is less important. Thus, F$^+$ ions originating from Si reacted with XeF$_2$ are emitted after direct excitation of both the anion F 2s and the cation Si 2p core-level electrons. However, for Cl attached to Si, which is an even more covalent system, excitation of anion Cl 3s electrons produces Cl$^+$ ion desorption, while excitation of cation Si 2p core electrons does not. This is because, for a fairly covalent bond, the Si 2p core hole can be quickly filled by an intra-atomic process, which does not lead to a two-hole repulsive state and thereby quenches the production of ions. This intra-atomic decay is possible because of the smaller amount of charge transfer from the Si cation to the Cl anion, as compared to Si–F.

Acknowledgements

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